

# **AGGLOMERATION CONTROL USING EARLY TRANSITION METAL ALLOYS**

## **TECHNICAL FIELD OF THE INVENTION**

[0001] The present invention relates generally to fabrication of integrated circuit devices, and in particular to the use of early transition metal alloys and their nitrides to reduce the agglomeration tendencies of metals used to form interconnects and other conductors within an integrated circuit device.

## **BACKGROUND OF THE INVENTION**

[0002] In the fabrication of a semiconductor integrated circuit device, it is desirable to fabricate the device with materials having a low resistivity (i.e., property of resistance to current flow) in order to optimize the device's electrical performance. Lower resistance within the device allows faster processing of information due to a smaller delay time associated with resistance to current flow.

[0003] Various portions of an integrated circuit device are typically interconnected using metal lines (i.e., conductive layers) with metal contacts extending to active areas within the device. Resistivity of the metal lines plays an increasingly important role in the overall resistance of an integrated circuit device. As such devices become more dense, wiring length increases. Furthermore, wiring pitch decreases, which effectively decreases the available wiring width. As the wiring width decreases, resistivity of the wiring material becomes a dominant factor as compared to parasitic capacitance between wires (i.e., that associated with device resistance). Thus, it is desirable to decrease the resistivity of wiring material within an integrated circuit device.

[0004] Copper (Cu) and silver (Ag) are becoming increasingly desirable in integrated circuit fabrication as a replacement for aluminum (Al), particularly for interconnect lines and other conductive structures (i.e., conductive digit lines and plugs connecting the conductive layers). Copper and silver have lower resistivity and higher resistance to

electromigration (i.e., the transport of metal atoms in conductors carrying large current densities, resulting in morphological degradation of the conductors) than aluminum.

[0005] These metal interconnects and contacts are typically formed using a dual damascene technique. In a dual damascene process, a dielectric layer is formed over a semiconductor substrate in which the integrated circuit device is being fabricated. Vias are formed in the dielectric layer to expose active areas of the semiconductor substrate and trenches are formed in the dielectric layer to couple the vias to other portions of the integrated circuit device. A metal layer is then blanket deposited to fill the trenches and vias and to cover the dielectric layer. The excess metal overlying the dielectric layer is removed, such as by chemical-mechanical planarization (CMP) to define the metal interconnects as the metal-filled trenches and metal contacts as the metal-filled vias. A CMP process generally involves abrading the surface of the semiconductor substrate with an abrasive and a solution to chemically assist the abrasive. The abrasive/solution combination is generally specific to the material to be removed and to the surrounding materials to be retained.

[0006] To reduce migration or diffusion of copper or silver into the underlying substrate, a diffusion barrier layer is often interposed between the substrate and the metal layer. Tantalum nitride is one material used as a diffusion barrier layer between the substrate and the metal layer. Continuous copper and silver layers are readily formed over tantalum nitride. However, it is generally necessary to use two different abrasive/solution combinations to first remove the copper or silver layer and then remove the tantalum nitride layer. While the use of titanium nitride as a diffusion barrier layer facilitates the use of a single abrasive/solution combination, it can be difficult to form copper or silver layers on a titanium nitride layer. Because of their large surface energies, copper and silver tend to agglomerate on a titanium nitride layer, thus tending to result in a discontinuous film and the production of voids in the damascene structure.

[0007] For the reasons stated above, and for other reasons stated below that will become apparent to those skilled in the art upon reading and understanding the present specification, there is a need in the art for alternative structures and methods for utilizing



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[0011] For yet another embodiment, the invention provides a method of forming a portion of an integrated circuit device. The method includes forming a layer of titanium nitride and forming a first metal layer on the layer of titanium nitride. The first metal layer contains a silver-rich alloy containing scandium, yttrium or lanthanum. Some examples include  $\text{Ag}_4\text{Sc}$  or  $\text{Ag}_4\text{Y}$ . The method further includes forming a second metal layer on the first metal layer, wherein the second metal layer contains silver.

[0012] For a further embodiment, the invention provides a method of forming a metal interconnect in an integrated circuit device. The method includes forming a diffusion barrier layer on a substrate and forming a nitrided metal layer on the diffusion barrier layer. The nitrided metal layer contains a first metal component, a second metal component capable of forming a crystalline compound with the first metal component, and nitrogen. The second metal component has a surface energy lower than a surface energy of the first metal component and the nitrided metal layer is rich in the first metal component. The method further includes forming a second metal layer on the nitrided metal layer, wherein the second metal layer contains the first metal component. Excess portions of the second metal layer are removed to define the metal interconnect.

[0013] For a still further embodiment, the invention provides a method of forming a portion of an integrated circuit device. The method includes forming a layer of titanium nitride and forming a nitrided metal layer on the layer of titanium nitride. The nitrided metal layer is of the form  $\text{MT}_x\text{N}_y$ , where M is a first metal component, T is a Group IIIA or Group IVA transition metal, N is nitrogen,  $x$  is an atomic fraction of T,  $y$  is an atomic fraction of N, and  $x$  and  $y$  are each less than one. The method further includes forming a metal layer on the nitrided metal layer, wherein the metal layer contains the first metal component.

[0014] For one embodiment, the invention provides a portion of an integrated circuit device. The portion includes a diffusion barrier layer and a first metal layer on the diffusion barrier layer. The first metal layer contains a crystalline alloy compound containing a first metal component and a second metal component, wherein the second metal component is selected from the group consisting of Group IIIA and Group IVA

elements. An atomic ratio of the first metal component to the second metal component in the first metal layer is greater than one. The portion further includes a second metal layer on the first metal layer, wherein the second metal layer contains the first metal component. The diffusion barrier layer may be a titanium-containing material such as titanium nitride.

[0015] For another embodiment, the invention provides a portion of an integrated circuit device. The portion includes a diffusion barrier layer and a nitrided metal layer on the diffusion barrier layer. The nitrided metal layer contains a first metal component, a second metal component and nitrogen. The second metal component is selected from the group consisting of Group IIIA and Group IVA elements. An atomic ratio of the first metal component to the second metal component in the nitrided metal layer is greater than one. The portion further includes a second metal layer on the first metal layer, wherein the second metal layer contains the first metal component. The diffusion barrier layer may be a titanium-containing material such as titanium nitride.

[0016] For yet another embodiment, the invention provides a portion of an integrated circuit device. The portion includes a titanium nitride layer and a nitrided metal layer on the titanium nitride layer. The nitrided metal layer contains copper, a metal component capable of forming a crystalline compound with the copper, and nitrogen. The metal component is selected from the group consisting of scandium, yttrium, lanthanum, titanium, zirconium and hafnium. An atomic ratio of copper to the metal component in the nitrided metal layer is greater than one. The portion further includes a layer of metal on the nitrided metal layer, wherein the layer of metal contains copper.

[0017] For still another embodiment, the invention provides a portion of an integrated circuit device. The portion includes a titanium nitride layer and a nitrided metal layer on the titanium nitride layer. The nitrided metal layer contains silver, a metal component capable of forming a crystalline compound with the silver, and nitrogen. The metal component is selected from the group consisting of scandium, yttrium and lanthanum. An atomic ratio of silver to the metal component in the nitrided metal layer is greater than one. The portion further includes a layer of metal on the nitrided metal layer, wherein the layer of metal contains silver.

[0018] Further embodiments of the invention include apparatus and methods of varying scope.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

[0019] Figures 1A-1F are cross-sectional views of a portion of an integrated circuit device at various stages of fabrication in accordance with one embodiment of the invention.

[0020] Figure 2 is a binary phase diagram for a copper-scandium binary system.

### **DETAILED DESCRIPTION**

[0021] In the following detailed description of the present embodiments, reference is made to the accompanying drawings that form a part hereof, and in which is shown by way of illustration specific embodiments in which the invention may be practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention, and it is to be understood that other embodiments may be utilized and that process, electrical or mechanical changes may be made without departing from the scope of the present invention. The terms wafer or substrate used in the following description include any base semiconductor structure. Examples include silicon-on-sapphire (SOS) technology, silicon-on-insulator (SOI) technology, thin film transistor (TFT) technology, doped and undoped semiconductors, epitaxial layers of a silicon supported by a base semiconductor structure, as well as other semiconductor structures well known to one skilled in the art. Furthermore, when reference is made to a wafer or substrate in the following description, previous process steps may have been utilized to form regions/junctions in the base semiconductor structure, and the terms wafer and substrate include the underlying layers containing such regions/junctions. The following detailed description is, therefore, not to be taken in a limiting sense, and the scope of the present invention is defined only by the appended claims and equivalents thereof.

[0022] Figures 1A-1F are cross-sectional views of a portion of an integrated circuit device 100 at various stages of fabrication. In Figure 1A, a dielectric layer 110 is formed on a base layer 105. For one embodiment, the base layer 105 is a semiconductor substrate, such as a monocrystalline silicon substrate. Other semiconductor substrates are known and used in the art of semiconductor fabrication. For additional embodiments, the base layer 105 may be conductor layer. For example, the base layer 105 may be a metal line or other conductive interconnect, such as a Metal 1 layer, Metal 2 layer, Metal 3 layer, etc.

[0023] Dielectric layer 110 contains an insulator or dielectric material, such as a silicon oxide ( $\text{SiO} / \text{SiO}_2$ ), silicon nitride ( $\text{SiN} / \text{Si}_2\text{N} / \text{Si}_3\text{N}_4$ ) or silicon oxynitride ( $\text{SiO}_x\text{N}_y$ ) material. For one embodiment, the dielectric layer 110 contains a doped silicon oxide material, such as borophosphosilicate glass (BPSG), a boron- and phosphorous-doped silicon dioxide material. Other dielectric materials are known and used in the art of semiconductor fabrication.

[0024] The dielectric layer 110 is patterned to define recesses or apertures such as trenches 112 and vias 114 as depicted in Figure 1A. Patterning of the dielectric layer 110 may include conventional photolithographic techniques to mask portions of the dielectric layer 110 and to expose portions of the dielectric layer 110 where future trenches 112 and vias 114 are to be formed. The exposed portions of the dielectric layer 110 are then removed. The portions of the dielectric layer 110 may be removed by etching or other suitable removal technique known in the art. Removal techniques are generally dependent upon the material of construction of the layer to be removed as well as the surrounding or underlying layers to be retained.

[0025] Due to the nature of the dual damascene process, the depth of the etch is variable across the surface of the device 100, e.g., the etch depth is greater where vias 114 are defined and less where only trenches 112 are defined. Thus, two mask and etch steps can be utilized in a conventional photolithographic process to define the vias 114 separately from the trenches 112. Alternatively, a gray mask pattern can be utilized to define the vias 114 and trenches 112 simultaneously in one photolithographic mask and

etch step. The trenches 112 will form interconnect lines for the integrated circuit device while the vias 114 will form contacts to active areas of the integrated circuit.

[0026] Following patterning of the dielectric layer 110, a diffusion barrier layer 115 is formed overlying the dielectric layer 110 and the exposed portions of the base layer 105 in Figure 1B. The diffusion barrier layer 115 preferably covers the sidewalls and bottoms of the trenches 112 and vias 114 as well as the surface of the dielectric layer 110. Portions of the diffusion barrier layer 115 covering bottoms of the vias 114 are in contact with the underlying base layer 105, which may be an active area of a semiconductor substrate of the integrated circuit device 100 or an underlying interconnect of the integrated circuit device 100. For one embodiment, the diffusion barrier layer 115 is a titanium-containing layer. For a further embodiment, the diffusion barrier layer 115 is a titanium nitride layer.

[0027] An agglomeration control layer 120 is formed on the diffusion barrier layer 115 as a metal layer or a nitrided metal layer. For one embodiment, the agglomeration control layer 120 contains an early transition metal alloy of the form  $MT_x$ , where M is a first metal component, T is a Group IIIA or Group IVA transition metal and  $x$  is the atomic fraction of T. These early transition metal alloys contain a first metal component, M, that will be found in a subsequently-formed metal layer. For example, where copper (Cu) will be used as the major component of the interconnect structure, the first metal component of the agglomeration control layer 120 is chosen to be copper. Additional examples for the first metal component include noble and near noble metals such as silver (Ag), gold (Au), palladium (Pd), platinum (Pt), rhenium (Rh), iridium (Ir), ruthenium (Ru) and osmium (Os). Preferred metals for the interconnects and contacts typically have a high surface energy, which leads to difficulties in forming continuous layers due to a tendency to agglomerate during or after deposition.

[0028] The early transition metal alloys further contain a second metal component having a low surface energy relative to the metals used for the interconnects and contacts. The second metal component is a Group IIIA or Group IVA element as designated by the traditional IUPAC version of the periodic table. Such Group IIIA elements include scandium (Sc), yttrium (Y) and lanthanum (La). Such Group IVA elements include



titanium (Ti), zirconium (Zr) and hafnium (Hf). Note that other versions of the periodic table are known using different designations for these same groups. The second metal component is capable of forming stable crystalline compounds with the first metal component. The early transition metals of Group IIIA and Group IVA have low surface energies, thus permitting improved adhesion to the underlying diffusion barrier layer 115.

[0029] The agglomeration control layer 120 is rich in the first metal component, i.e., the atomic ratio of the first metal component to the second metal component is greater than one. For better adhesion to the subsequent metal layer, the atomic ratio of the first metal component to the second metal component in the agglomeration control layer 120 is preferably greater than two.

[0030] For one class of embodiments using copper for the interconnects and contacts, the early transition metal alloys are copper-rich alloys containing copper and at least one Group IIIA or Group IVA element capable of forming a stable crystalline compound with copper. Such stable crystalline compounds can be readily determined from binary alloy phase diagrams of the two compounds of interest. For example, Figure 2 is a binary phase diagram for the copper-scandium binary system as reported in Binary Alloy Phase Diagrams: Second Edition, Massalski, T.B., *editor*, The Materials Information Society, 1990. From Figure 2, it can be seen that stable crystalline structures or equilibrium phases are found as Cu, Cu<sub>4</sub>Sc, Cu<sub>2</sub>Sc, CuSc, αSc and βSc. From these stable crystalline structures, Cu<sub>4</sub>Sc and Cu<sub>2</sub>Sc are copper-rich alloys and thus suitable for use with various embodiments. For alloys of other binary systems, appropriate binary alloy phase diagrams can be obtained or generated in order to identify stable crystalline structures.

[0031] For one embodiment, the agglomeration control layer 120 is a copper-rich alloy containing Cu<sub>4</sub>Sc. For another embodiment, the agglomeration control layer 120 is a copper-rich alloy containing Cu<sub>6</sub>Y. For yet another embodiment, the agglomeration control layer 120 is a copper-rich alloy containing Cu<sub>4</sub>Ti. For still another embodiment, the agglomeration control layer 120 is a copper-rich alloy containing Cu<sub>3</sub>Ti. For a further embodiment, the agglomeration control layer 120 is a copper-rich alloy containing Cu<sub>5</sub>Zr.

[0032] For another class of embodiments using silver for the interconnects and contacts, the early transition metal alloys are silver-rich alloys containing silver and at least one Group IIIA element capable of forming a stable crystalline compound with silver. For one embodiment, the agglomeration control layer 120 is a silver-rich alloy containing  $\text{Ag}_4\text{Sc}$ . For another embodiment, the agglomeration control layer 120 is a silver-rich alloy containing  $\text{Ag}_4\text{Y}$ .

[0033] The crystalline alloy portions of the agglomeration control layer 120 generally provide reduced surface energies relative to amorphous films of the same metal components. This leads to improved adhesion between the agglomeration control layer 120 and the underlying diffusion barrier layer 115. Because crystalline alloy structures are more stable than amorphous alloys, crystalline alloys are also easier to fabricate with high levels of repeatability relative to amorphous alloys of the same metal components. Ease of fabrication and repeatability are important factors in reducing the cost of the integrated circuit device and in increasing its reliability.

[0034] Another consideration in the fabrication of the agglomeration control layer 120 is its electrical resistance. In general, higher levels of the first metal component will lead to lower resistance levels of the agglomeration control layer 120 and improved device performance. While crystalline alloy portions of the agglomeration control layer 120 provide improved adhesion to the underlying diffusion barrier layer 115, it is not necessary that the agglomeration control layer consist solely of crystalline structures of the first and second metal components. Regions of crystalline alloy structures can serve as nuclei for the growth of regions containing the first metal component in a substantially pure or elemental state. These regions of crystalline alloy structures provide the desired adhesion between the first metal component and the diffusion barrier layer 115. Thus, for additional embodiments, the agglomeration control layer 120 contains an amount of the first metal component in its elemental state. For one embodiment, at least 25 wt% of the agglomeration control layer 120 is the first metal component in its elemental state. For another embodiment, at least 50 wt% of the agglomeration control layer 120 is the first metal component in its elemental state. For a further embodiment, the atomic ratio of the

first metal component to the second metal component is greater than 10. For a still further embodiment, the atomic ratio of the first metal component to the second metal component is greater than 20.

[0035] The agglomeration control layer 120 is preferably formed by physical vapor deposition (PVD) techniques. Examples include thermal evaporation, electron-beam evaporation and sputtering techniques well known in the art. PVD techniques are preferred as the crystalline structure is easily maintained during formation of the agglomeration control layer. A target, ingot or other source containing the crystalline alloy compound can be molded, pressed or otherwise formed for use in the chosen PVD technique.

[0036] For embodiments having an atomic ratio of the first metal component to the second metal component higher than the atomic ratio in the crystalline alloy compound, the PVD source may be a composite source containing a first portion of the crystalline alloy compound and a second portion of a material having increased levels of the first metal component, preferably other stable crystalline structures of the binary system and more preferably the first metal component in its elemental state. The first and second portions of the composite source are preferably intermixed to more easily form an agglomeration control layer 120 having a uniform composition. For example, a PVD source could be pressed from powdered  $\text{Cu}_4\text{Sc}$  and pure copper to produce a composite source having an atomic ratio of copper to scandium of greater than four to one.

[0037] The composite source may further contain more than two metal components. For example, the composite source may contain a first metal component in its elemental state, a first crystalline alloy compound of the first metal component and a Group IIIA or Group IVA element, and a second crystalline alloy compound of the first metal component and a different Group IIIA or Group IVA element. PVD sources may further contain additional components that do not materially affect the basic and novel properties of the agglomeration control layers disclosed herein.

[0038] For one embodiment, the agglomeration control layer 120 contains an early transition metal alloy nitride. Metal alloy nitrides containing the first and second metal

components are generally more robust at higher temperatures than their corresponding metal alloy. To produce a metal alloy nitride, the PVD process can be carried out in an atmosphere containing nitrogen ( $N_2$ ). For example, the agglomeration control layer 120 can be formed by a reactive sputtering process using a target containing a crystalline alloy compound rich in the first metal component. During the reactive sputtering process, a nitrogen-containing atmosphere is created in the deposition chamber. The nitrogen-containing atmosphere preferably contains nitrogen and a noble or inert gas, e.g., argon (Ar). The nitrogen reacts with the first and second metal components in the target during deposition to form a metal alloy nitride of the form  $MT_xN_y$ , where M is the first metal component, T is a Group IIIA or Group IVA transition metal of the second metal component, N is nitrogen,  $x$  is the atomic fraction of T and  $y$  is the atomic fraction of N. For a further embodiment, the nitrogen-containing atmosphere contains approximately 5% to 30% nitrogen by volume.

[0039] Following formation of the agglomeration control layer 120, a metal layer 130 is formed. The metal layer 130 is generally formed as a blanket deposition in dual damascene techniques. This fills the trenches 112 and vias 114 by covering the entire surface of the dielectric layer 110 with the metal layer 130. The metal layer 130 may be formed using chemical vapor deposition (CVD) or physical vapor deposition (PVD) techniques. Additionally, the metal layer 130 may be formed using electroplating techniques, which may include first forming an optional seed layer 125 overlying the agglomeration control layer 120, as shown in Figure 1D, followed by electroplating the remaining portion of the metal layer 130 onto the seed layer 125 resulting in the structure shown in Figure 1E. The seed layer 125 contains the first metal component. For one embodiment, the seed layer 125 consists essentially of the first metal component.

[0040] Electroless plating is another example of a process that may be used to form the metal layer 130 covering the surface of the integrated circuit device 100. The metal layer 130 contains the first metal component of the agglomeration control layer 120. For example, where the first metal component of the agglomeration control layer 120 contains copper, silver, gold, palladium, platinum, rhenium, iridium, ruthenium or osmium, the



